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Original research paper

Synthesis of anode active material particles for lithium-ion batteries by surface modification via chemical vapor deposition and their electrochemical characteristics

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ABSTRACT

The high capacity and optimal cycle characteristics of silicon render it essential in lithium-ion batteries. We have attempted to realize a composite material by coating individual silicon (Si) particles of μm-order diameter with a silicon oxide film to serve as an active material in the anode of a lithium-ion battery and thus improve its charge-discharge characteristics. The particles were coated using an inductively coupled plasma-chemical vapor deposition (ICP-CVD) process that realized a homogeneously coated silicon oxide film on each Si particle. The film was synthesized using **t**etra**e**thyl **o**rtho**s**ilicate (TEOS) with hydrogen (H_2) gas used as a reducing agent to deoxidize the silicon dioxide. This enabled the control of the silicon oxidation number in the layers produced by adjusting the H_2 flow during the silicon oxide deposition by ICP-CVD. The silicon oxide covering the Si particles included both silicon monoxide and suboxide, which served to improve the charge-discharge characteristics. We succeeded in realizing an active material using Si, which is abundant in nature, for the anode of a lithium-ion battery with highly charged, improved cycle properties.

1. Introduction

Because of its high theoretical lithium storage capability of about 4000 mAh/g [1], silicon is one of the most attractive anode materials for lithium-ion batteries. However, the drastic changes in volume that silicon often undergoes during charge-discharge cycles have prevented silicon anodes from being used in lithium-ion secondary batteries [2]. To overcome this problem, various modifications, such as the use of nanostructured silicon anodes [3], the synthesis of composites with other materials [4] and the use of carbon coatings [5], have been suggested. The use of silicon monoxide as an alternative anode material has been proposed because silicon monoxide exhibits little change in its volume and high conductivity [6–11]. However, the capacity of silicon monoxide is about 1200 mAh/g [12–13], which is lower than that of other potential materials. Numerous studies have been carried out to explore ways of compensating for this by combining silicon monoxide with other materials [14–17]. In this study, we consider a technique that reduces the cracking due to changes in volume while affecting the capacity as little as possible; Si particles are formed in the core of a suitable material and the possible collapse of the crystal structure of Si is prevented by forming silicon monoxide around the Si particles.

For the synthesis of silicon monoxide around Si particles, both the dry processes of vacuum evaporation and sputtering and the wet process of using a mixture of Si or silicon monoxide with a solvent or sol-gel were considered. However, for these formation processes, the charge-discharge characteristics of Si particles with a suboxide synthesized at a low growth temperature would be unlikely to meet the desired standard as the formation of a stable silicon monoxide film with a low glass transition temperature is difficult.

Chemical vapor deposition with inductively coupled plasma (ICP-CVD) was considered most likely to create a suitable coating in the form of a synthesized silicon oxide layer. The energy of the plasma source of inductively coupled plasma is supplied by electromagnetic induction using a time-varying magnetic field produced by an electrical current in a helical spring. The results of other studies involving such synthesis by ICP-CVD have been reported extensively [18–23].

Although ICP-CVD is typically used for the synthesis of silicon oxide, silicon dioxide can be produced by chemical vapor deposition with a gaslike silicon-containing compound. It was therefore expected that an oxide film with a low silicon oxidation number could be formed by mixing a reducing gas with steam from an

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organic liquid including a silicon compound. A high-diffusibility gas was used to obtain good coverage on all the Si particles without any need for agitation.

2. Experimental

In this study, we developed a growth method in which Si particles, which had an average diameter of 3.8 μm and a purity of 99.999% (Kojundo Chemistry Laboratory Co., Ltd., Japan), could pass into a plasma atmosphere, resulting in their coating with a silicon suboxide film with satisfactory coverage. Fig. 1(a) shows a schematic diagram of the ICP-CVD setup with an additional remote plasma system for plasma activation in a processing vessel, and Fig. 1(b) shows a photograph taken while operating the plasma. The remote plasma system was excited by a helicon wave emitted from a helical spring charged by electrical power at a high frequency. An advantage of this system is that the plasma excitation can be easily maintained at normal air pressure. Atomized **T**etra-**e**thyl **o**rtho**s**ilicate (TEOS; $(Si(OHC_2H_5)_4)$) with Ar carrier gas, used as seeds to promote silicon oxidation, and hydrogen (H_2), used as the reducing agent gas in the oxidization process, were injected into the processing vessel, where they reacted with argon (Ar) as a carrier gas and radicals in the plasma. The growth temperature of silicon oxide using TEOS reached nearly 800 K in the chemical vapor deposition process.

Fig. 2 shows the dependence of the Ar gas pressure on the power when the plasma was excited, and Fig. 3 shows the dependence of the temperature of the Si powder on the Ar gas pressure when the plasma was excited. The temperature in the vessel was measured by a thermocoupler and is indicated in Fig. 3 as Tg. The temperature near the exhaust port of the vessel during plasma excitation is indicated by Ts. At temperatures over 900 K, it has been reported that a silicon monoxide or a composite with a monoxide content tends to occur disproportionately with resulting in the formation of silicon dioxide and elementary silicon [24]. Though it is important to keep the temperature somewhat lower to obtain a stable silicon monoxide or semi-silicate, it is difficult to control the content as they tend to grow inhomogeneously.

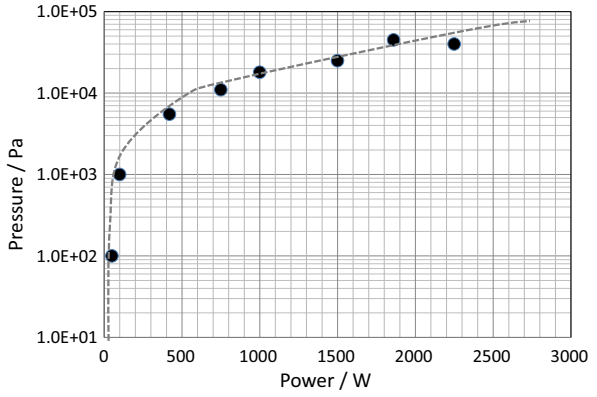

Fig. 2. Dependence of pressure in silica cylinder with Ar gas on power supplied to the coil during plasma excitation.

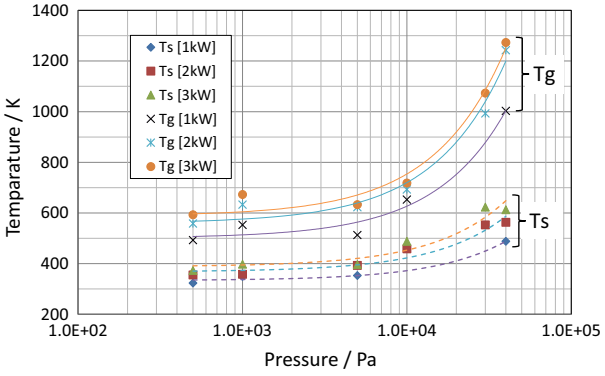

Fig. 3. Dependence of temperature of Si powder in the silica cylinder (Tg) and near the exhaust port (Ts) on Ar gas pressure during plasma excitation.

Therefore, the optimal growth temperature of silicon oxide by TEOS which provides the desired content is near 800 K using ICP-CVD.

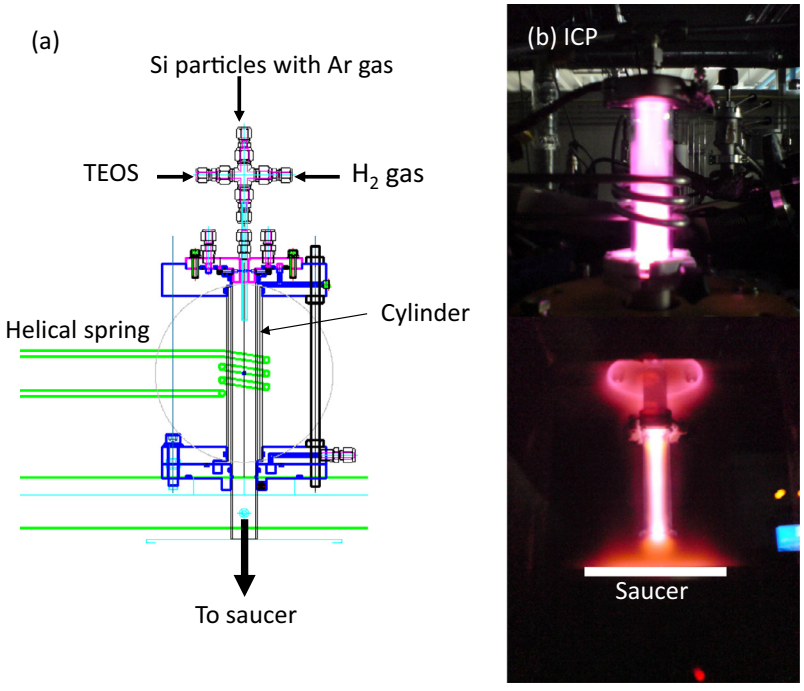

Fig. 1. Schematic diagram of ICP-CVD setup (a) and photograph taken during plasma excitation in the ICP setup (b).

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